

## LONG WEARING EMULSION COMPOSITION FOR MAKING UP EYES AND SKIN

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### Technical Field

The invention is in the field of compositions for application to eyebrows and eyelashes to impart color, or for use in lining the eyes with color, or application to the skin as in a facial or body tattoo, or to the lips as a lip color.

### Background of the Invention

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Many women use a variety of products to beautify the eyes, including brow color, eyeshadow, mascara, and eyeliner. Such products accentuate the eyes and in the case of lash products, will also give the appearance of longer lashes.

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One of the common problems with eye products such as liners and mascara is that they often do not wear for long periods of time and have a tendency to smudge. With respect to eyeliner, more adventurous consumers have addressed this problem by having "permanent" eyeliner essentially tattooed onto the eyelids. This is a permanent cosmetic procedure and the eyeliner is not removable.

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Cosmetic manufacturers are constantly exploring new formulas for such products that will fill the need gaps of longer wear and reduced smudging in a way that will not necessitate visits to beauty salons to have permanent cosmetics tattooed into the skin. The desired cosmetics should provide long lasting, durable wear, preferably one or more days, and be removable by the consumer whenever desired. In addition, the color should be rich and as natural looking as possible.

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Typically, products for making up the eyes contain inorganic iron oxide pigments in an emulsion. Iron oxides are water insoluble and are generally ground with one or

more oils in the composition to form what is referred to as a pigment grind. For example, traditional mascaras are mixtures of waxes, oils, and inorganic pigments. They may be anhydrous or in the emulsion form. Many of the so-called water resistant mascaras are anhydrous while traditional mascaras are often in the emulsion form. These types of

5 mascaras are generally applied to the lashes and wear for periods of time ranging from several hours to one day. Users usually remove what remains of such products at the end of the day by washing with water. Another problem associated with such mascaras is their tendency to smudge when the user becomes warm or wears eye makeup that is oily. Moreover, since such products contain significant levels of wax and oil, the inorganic

10 pigments that provide color may tend to be muted. This in turn provides a more artificial look to mascara coated lashes.

Similarly, eyeliner is usually a liquid product or in a pencil form. It is applied to the upper and lower lids to accentuate the eye area. While eyeliner is a very desirable beauty product, it tends to smudge very readily, especially when worn on lower lashes.

15 The smudging is due, in part, to the solubilizing of the dried eyeliner formula by skin oils, perspiration, and tears. Again, the iron oxides typically used to provide color to such products are muted and matte in tone, sometimes providing an artificial look to the liner especially when the color is very dark.

The major need gaps in the field of lash, brow, lip, and liner products relates to

20 creating a color that has a rich, deep, natural tone, and at the same time providing a product that has the capability of extended wear (one or more days) if desired by the consumer, and where negative tendencies such as smudging upon exposure to perspiration, tears, and environmental assaults are reduced or eliminated.

Organic pigments are well known for use in cosmetic compositions. They are particularly desirable because the colors provide a very rich intensity that is not found with traditional inorganic pigments. However, because most organic colors are water soluble, it is difficult to incorporate them into long wearing cosmetics because if the cosmetic user comes into contact with the water such as perspiration, raindrops, etc. the organic pigments readily dissolve in the water and tend to run on the skin and hair. Further, organic pigments are generally not compatible in non-aqueous systems at any appreciable concentration, so they cannot be used in amounts large enough to impart significant color to the composition.

The object of the invention is to prepare emulsion products for making up the eyes and skin, such as mascara compositions (or lash tints), brow color, eyeliner, lip color, facial or body tattoos that exhibit extended wear, look natural, provide a rich color, and exhibit reduced smudging.

Another object of the invention is to provide emulsion eye or face products that are capable of wearing for one to five days and provide a natural appearance.

Another object of the invention is to provide commercially acceptable, stable, emulsion products for making up the eyes where the color is obtained with the use of organic pigments.

#### Summary of the Invention

The invention comprises a water and oil emulsion composition for making up the eyes and skin comprising at least one film forming polymer and at least one organic pigment forming the main color component of the composition, said composition being free of inorganic pigments.



be different when a sample of that composition is drawn across the back of the hand, for example, and visually observed with the naked eye. Preferably, the organic pigments provide at least about 0.1-95%, preferably at least about 45-80%, most preferably at least about 80-90% of the color of the claimed composition. In the most preferred embodiment, the organic pigments provide about 100% of the color of the claimed composition (meaning that when the entire pigment concentration is measured, the percentage of organic pigments in the entire pigment load is reflected in the percentage mentioned). It is possible that the claimed compositions may contain one or more inorganic pigments including but not limited to metal oxides such as titanium, iron, oxides such as black, red, yellow, green, and blue, and similar organic powders.

Certain preferred compositions are free of natural and synthetic waxes. Certain more preferred compositions are free of organic, solid, non-polymeric oil phase gelling agents. The term "solid" means that the gelling agent is a solid at room temperature. The term "gelling agent" means an ingredient that is included in the composition for the purpose of gelling, or increasing the viscosity of the composition from a liquid state to a less liquid or more solid state. The term "oil phase" when used in describing the organic, solid, non-polymeric oil phase gelling agent means that the gelling agent is soluble in the oil phase of the emulsion composition. Examples of organic, solid, non-polymeric gelling agents are described in U.S. Patent No. 6,214,329 which is hereby incorporated by reference in its entirety. In particular, the claimed compositions are free of organic, solid, non-polymeric gelling agents such as fatty acids, fatty acid esters, N-acyl amino acids, or esters or amides thereof; 12-hydroxystearic acid and esters and amides thereof; fatty acid esters of di- or trifunctional alcohol dimers; alkylamides of di- and

tricarboxylic acids; or mixtures thereof. The term "free of" means that the compositions do not contain any appreciable amount of the solid, organic, non-polymeric agent, e.g. less than about 5%, preferably less than about 1%. Most preferred is where the compositions do not contain a wax, and/or a solid, organic, non-polymeric gelling agent.

5 I. The Water Phase

The claimed compositions are in the form of a water-in-oil or oil-in-water emulsion. The range and content of the oil and water phases will depend on the pigments and other ingredients used, and wide ranges of both phases are suitable provided the emulsion is stable and commercially acceptable. Preferred ranges are about 0.1-95% water and about 0.1-99.9% oil, all percentages by weight of the total composition. Preferably, the emulsion is a water in oil emulsion comprising about 0.001-50%, preferably 0.01-25%, more preferably 0.0-10% by weight of the total composition of water, and about 50-99.999%, preferably 75-99.99%, more preferably 90-99.9% by weight of the total composition of oil.

15 II. Pigments and Particulate Fillers

A. Organic Pigments

The composition of the invention preferably comprises about 0.05-30%, preferably about 0.1-25%, more preferably about 0.5-20% by weight of the total composition of one or more water soluble or water insoluble organic pigments or salts thereof. If the organic pigments are water insoluble (e.g. the Lakes), the organic pigments should be dispersible in the oil phase of the emulsion. In the event the organic pigments are water soluble, they should be soluble in the water phase of the emulsion. Particularly preferred are water soluble organic pigments that are red, green, blue, yellow,

violet, orange, and mixtures thereof, or the water insoluble Lakes of such pigments, which means that the water soluble organic pigment is reacted with one or more metal salts such as calcium, aluminum, barium, zirconium, and the like to form salts.

Particularly preferred water insoluble organic pigments are the aluminum Lakes of the

5 organic pigments, which is where the organic pigment is reacted with aluminum to form the water insoluble aluminum salt. Formation of the metal salt of the organic pigment will generally convert the pigment from a water soluble pigment into a water insoluble pigment. Examples of organic pigment families that may be used herein include azo, (including monoazo and diazo), fluoran, xanthene, indigoid, triphenylmethane,

10 anthroquinone, pyrene, pyrazole, quinoline, quinoline, or metallic salts thereof. Preferred are D&C colors, FD&C colors, or Lakes of D&C or FD&C colors. The term "D&C" means drug and cosmetic colors that are approved for use in drugs and cosmetics by the FDA. The term "FD&C" means food, drug, and cosmetic colors which are approved for use in foods, drugs, and cosmetics by the FDA. Certified D&C and FD&C colors are  
15 listed in 21 CFR 74.101 et seq. and include the FD&C colors Blue 1, Blue 2, Green 3, Orange B, Citrus Red 2, Red 3, Red 4, Red 40, Yellow 5, Yellow 6, Blue 1, Blue 2; Orange B, Citrus Red 2; and the D&C colors Blue 4, Blue 9, Green 5, Green 6, Green 8, Orange 4, Orange 5, Orange 10, Orange 11, Red 6, Red 7, Red 17, Red 21, Red 22, Red 27, Red 28, Red 30, Red 31, Red 33, Red 34, Red 36, Red 39, Violet 2, Yellow 7, Yellow  
20 8, Yellow 10, Yellow 11, Blue 4, Blue 6, Green 5, Green 6, Green 8, Orange 4, Orange 5, Orange 10, Orange 11, and so on. Suitable Lakes of D&C and FD&C colors are defined in 21 CFR 82.51. Particularly preferred are Lakes formed by the reaction of the organic pigment with a metallic salt such as aluminum, calcium, zirconium, barium, and the like.

Suitable reds include pigments from the monoazo, disazo, fluoran, xanthene, or indigoid families or Lakes thereof, such as Red 4, 6, 7, 17, 21, 22, 27, 28, 30, 31, 33, 34, 36, and Red 40. Also suitable are Lakes of such red pigments. Typically the metal salts are aluminum, barium, and the like.

- 5            Suitable yellows include wherein the yellow pigment is a pyrazole, monoazo, fluoran, xanthene, quinoline, or salt thereof. Suitable yellows include Yellow 5, 6, 7, 8, 10, and 11, as well as Lakes of such yellow pigments.

Suitable violets include those from the anthroquinone family, such as Violet 2 and Lakes thereof. Examples of orange pigments are Orange 4, 5, 10, 11, or Lakes thereof.

- 10           Preferably, the organic pigments form the main color component of the invention meaning that the color of the composition is attributable to the organic pigments, however such organic pigments may be present alone or in combination with one or more inorganic pigments. In one particularly preferred embodiment of the invention the composition is a lash color that is rich dark brown or black in color, which is achieved  
15           through the use of a combination of organic pigments which are not black or brown in color. The rich deep brown or black color may be achieved by combining organic pigments or Lakes thereof in the red, green, yellow, blue, violet, and orange family. Preferably the lash tint comprises a mixture of red, green, yellow, and blue organic pigments or Lakes thereof and is deep brown or black in color. In the most preferred  
20           composition the pigments comprise a mixture of water soluble red, green, yellow, and blue organic pigments. These preferred compositions may comprise organic pigments in Lake form, however, since such pigments are water insoluble, they will be dispersed in the oil phase of the emulsion. The emulsion compositions may contain any combination



of water soluble and water insoluble pigments so long as the compositions are stable. The most preferred compositions of the invention are dark brown or black in color and are free of iron oxides, particularly black iron oxide, or contain such iron oxides in amounts less than about 5-10% by weight.

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#### B. Inorganic Pigments

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In the event the claimed composition contains inorganic pigments, preferred is where the amount is sufficient to accentuate the color achieved with the organic pigment but not obscure the intensity of the organic pigments. Preferred ranges include about 0.001-15%, preferably about 0.005-10%, more preferably about 0.01-8% by weight of the total composition. Suitable inorganic pigments include iron oxides such as red, blue, black, green, and yellow; titanium dioxide, bismuth oxychloride, and the like. Preferred are iron oxides. Such inorganic pigments may be found in the water or oil phases depending on their solubilities. For example, iron oxides are usually water soluble and will migrate to the oil phase. On the other hand, iron oxides treated with hydrophobic agents such as silicone, lecithin, mineral oil, or similar materials, will cause the pigment to be hydrophobic in nature and migrate to the oil phase of the composition.

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#### C. Particulate Fillers

It may also be desirable to include one or more particulate fillers in the claimed composition. If so, suggested ranges are about 0.001-40%, preferably about 0.05-35%, more preferably about 0.1-30% by weight of the total composition. Preferably, the particulate matter has a particle size of 0.02 to 100, preferably 0.5 to 100, microns. Such particulate fillers may be part of the oil or water phases, however it is preferred that they be incorporated into the oil phase whenever compatible therewith. Suitable particle

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fillers include titanated mica, fumed silica, spherical silica, polymethylmethacrylate, micronized teflon, boron nitride, acrylate copolymers, aluminum silicate, aluminum starch octenylsuccinate, bentonite, calcium silicate, cellulose, chalk, corn starch, diatomaceous earth, fuller's earth, glyceryl starch, hectorite, hydrated silica, kaolin, magnesium aluminum silicate, magnesium trisilicate, maltodextrin, montmorillonite, microcrystalline cellulose, rice starch, silk powder, silica, talc, mica, zinc laurate, zinc myristate, zinc rosinate, alumina, attapulgite, calcium carbonate, calcium silicate, dextran, kaolin, nylon, silica silylate, sericite, soy flour, tin oxide, titanium hydroxide, trimagnesium phosphate, walnut shell powder, or mixtures thereof. The above mentioned powders may be surface treated with lecithin, amino acids, mineral oil, silicone oil or various other agents either alone or in combination, which coat the powder surface and render the particles more lipophilic in nature.

### III. Oil Phase

The composition comprises about 0.1-85%, preferably about 5-80%, more preferably about 10-75% by weight of the total composition of an oil phase which may comprise one or more oils or other liquid materials soluble in the oil phase. A variety of ingredients may be suitable including volatile oils, nonvolatile oils, and mixtures thereof.

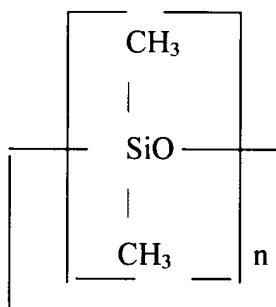
#### A. Volatile Liquids

The term "volatile" means that the oil has a measurable vapor pressure, or a vapor pressure of at least 2 mm. of mercury at 20° C. The term "nonvolatile" means that the oil has a vapor pressure of less than 2 mm. of mercury at 20° C. Preferably, the compositions of the invention contain a significant portion of volatile solvents as the liquid carrier. Suitable volatile oils are liquids, and enable easy formulation of the

composition of the invention. When the composition of the invention is applied to the desired surface, the volatile solvent of the invention must be capable of flashing off to leave the other ingredients in the composition affixed to the surface. Suitable volatile solvents generally have a viscosity of 0.5 to 10 centipoise at 25° C. Suitable volatile solvents include linear silicones, cyclic silicones, paraffinic hydrocarbons, or mixtures thereof.

### 1. Volatile Silicones

Cyclic silicones (or cyclomethicones) are of the general formula:



where n = 3-6.

Linear volatile silicones in accordance with the invention have the general formula:



where n=0-7, preferably 0-5.

Linear and cyclic volatile silicones are available from various commercial sources including Dow Corning Corporation and General Electric. The Dow Corning volatile silicones are sold under the tradenames Dow Corning 244, 245, 344, and 200 fluids. These fluids comprise octamethylcyclotetrasiloxane, decamethylcyclopentasiloxane, hexamethyldisiloxane, and mixtures thereof.

## 2. Paraffinic Hydrocarbons

Also suitable as the volatile liquid are various straight or branched chain paraffinic hydrocarbons having 5 to 40 carbon atoms, more preferably 8-20 carbon atoms. Suitable hydrocarbons include pentane, hexane, heptane, decane, dodecane, tetradecane, tridecane, and C<sub>8-20</sub> isoparaffins as disclosed in U.S. patent nos. 3,439,088 and 3,818,105, both of which are hereby incorporated by reference. Preferred volatile paraffinic hydrocarbons have a molecular weight of 70-225, preferably 160 to 190 and a boiling point range of 30 to 320, preferably 60-260 degrees C., and a viscosity of less than 10 cs. at 25 degrees C. Such paraffinic hydrocarbons are available from EXXON under the ISOPARS trademark, and from the Permethyl Corporation. Suitable C<sub>12</sub> isoparaffins are manufactured by Permethyl Corporation under the tradename Permethyl 99A. Another C<sub>12</sub> isoparaffin (isododecane) is distributed by Presperse under the tradename Permethyl 99A. Various C<sub>16</sub> isoparaffins commercially available, such as isohexadecane (having the tradename Permethyl R), are also suitable.

### B. Nonvolatile Liquids

The liquid carrier may also comprise low viscosity non-volatile liquid oils such as silicones, esters, and the like. If the nonvolatile oils are too heavy or greasy it may hamper the long wearing characteristics of the invention. Generally, the viscosity of the nonvolatile oils if present should range from about 11-1000, preferably less than 100 centipoise, most preferably less than about 50 centipoise at 25° C. Examples of such oils include polyalkylsiloxanes, polyarylsiloxanes, and polyethersiloxanes. Examples of such nonvolatile silicones are disclosed in Cosmetics, Science and Technology 27-104 (Balsam and Sagarin ed. 1972); and U.S. Patent Nos. 4,202,879 and 5,069,897, both of

which are hereby incorporated by references. Further nonlimiting examples of such silicones include dimethicone, phenyl trimethicone, dimethicone copolyol, and so on.

Also suitable are lower viscosity organic liquids including saturated or unsaturated, substituted or unsubstituted branched or linear or cyclic organic compounds  
5 that are liquid under ambient conditions. Preferred organic liquids include those described in U.S. Patent No. 5,505,937; 5,725,845; 5,019,375; and 6,214,329, all of which are incorporated by reference herein in their entirety.

In the preferred composition the oil phase comprises one or more nonvolatile oils either alone or in combination with one or more nonvolatile oils. Particularly preferred is  
10 where the liquid vehicle comprises a mixture of volatile silicone and volatile paraffinic hydrocarbons which serve as the carrier in which the organic pigments are dispersed.

#### IV. Film Forming Polymer

The composition preferably comprises 0.1-35%, preferably 0.5-30%, more preferably 1-25% by weight of the total composition of one or more film forming  
15 polymers. The film forming polymer (or film former) may be water soluble or water insoluble. Suitable film forming polymers are those that, when the composition is applied to the desired surface, form a film on the surface to which the composition is applied when the liquid in the composition evaporates. This causes the film forming polymer to form a film which holds the organic pigment particles in place with the  
20 network created by the hardened polymer. The term "soluble" means that the film forming polymer is soluble in the phase in question, and will form a single homogeneous phase when incorporated therein. For example, if the film forming polymer is oil soluble it will generally be soluble in the oil phase of the emulsion and when incorporated therein

the oil and the polymer will form a single homogeneous phase. Similarly, if the film forming polymer is water soluble, if incorporated in the water phase the polymer and the water will form a single homogeneous phase. It may also be possible for the emulsion to contain a film forming polymer that is soluble in one phase but is found dispersed in the other phase. For example, water soluble film forming polymer may be dispersed in the oil phase of the emulsion or an oil soluble polymer may be dispersed in the water phase of the emulsion. In short, any combination of film forming polymer and phase is suitable so long as the compositions are stable. The term "dispersible" means that the film forming polymer is readily dispersed in the liquid vehicle and forms a stable, heterogeneous composition where the dispersed polymer remains stable and suspended in the liquid vehicle and is compatible therewith (without settling out, for example). The film forming polymer also has adhesive properties, meaning that when incorporated into the claimed composition in any phase, and applied to the lashes, the film forming polymer forms a film or a weld on the lashes. Such a film will have adhesive and cohesive strength, as is understood by those skilled in the art.

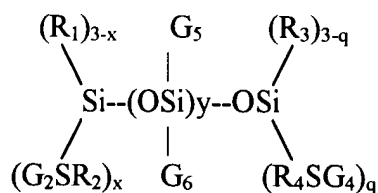
A variety of film forming polymers may be suitable so long as they are soluble or dispersible in, and compatible with, either phase of the emulsion, capable of forming a film on the surface to which it is applied, and may be removed with a remover; and compatible with the pigment and other ingredients in the composition. Such polymers may be natural or synthetic and are further described below.

#### A. Synthetic Polymers

##### 1. Copolymers of Silicone and Ethylenically Unsaturated Monomers

One type of film forming polymer that may be used in the compositions of the invention is obtained by reacting silicone moieties with ethylenically unsaturated monomers. These copolymers may be water soluble or oil soluble depending on the substituents that are found on the polymer. The resulting copolymers may be graft or block copolymers. The term "graft copolymer" is familiar to one of ordinary skill in polymer science and is used herein to describe the copolymers which result by adding or "grafting" polymeric side chain moieties (i.e. "grafts") onto another polymeric moiety referred to as the "backbone". The backbone may have a higher molecular weight than the grafts. Thus, graft copolymers can be described as polymers having pendant polymeric side chains, and which are formed from the "grafting" or incorporation of polymeric side chains onto or into a polymer backbone. The polymer backbone can be a homopolymer or a copolymer. The graft copolymers are derived from a variety of monomer units.

One type of polymer that may be used as the film forming polymer is a vinyl-silicone graft or block copolymer having the formula:



wherein  $G_5$  represents monovalent moieties which can independently be the same or different selected from the group consisting of alkyl, aryl, aralkyl, alkoxy, alkylamino, fluoroalkyl, hydrogen, and -ZSA; A represents a vinyl polymeric segment consisting essentially of a polymerized free radically polymerizable monomer, and Z is a divalent

linking group such as C<sub>1-10</sub> alkylene, aralkylene, arylene, and alkoxyalkylene, most preferably Z methylene or propylene.

G<sub>6</sub> is a monovalent moiety which can independently be the same or different selected from the group consisting of alkyl, aryl, aralkyl, alkoxy, alkylamino, fluoroalkyl, hydrogen, and -ZSA;

G<sub>2</sub> comprises A;

G<sub>4</sub> comprises A;

R<sub>1</sub> is a monovalent moiety which can independently be the same or different and is selected from the group consisting of alkyl, aryl, aralkyl, alkoxy, alkylamino, fluoroalkyl, hydrogen, and hydroxyl; but preferably C<sub>1-4</sub> alkyl or hydroxyl, and most preferably methyl.

R<sub>2</sub> is independently the same or different and is a divalent linking group such as C<sub>1-10</sub> alkylene, arylene, aralkylene, and alkoxyalkylene, preferably C<sub>1-3</sub> alkylene or C<sub>7-10</sub> aralkylene, and most preferably -CH<sub>2</sub>- or 1,3-propylene, and

R<sub>3</sub> is a monovalent moiety which is independently alkyl, aryl, aralkyl, alkoxy, alkylamino, fluoroalkyl, hydrogen, or hydroxyl, preferably C<sub>1-4</sub> alkyl or hydroxyl, most preferably methyl;

R<sub>4</sub> is independently the same or different and is a divalent linking group such as C<sub>1-10</sub> alkylene, arylene, aralkylene, alkoxyalkylene, but preferably C<sub>1-3</sub> alkylene and C<sub>7-10</sub> alkylene, most preferably -CH<sub>2</sub>- or 1,3-propylene.

x is an integer of 0-3;

y is an integer of 5 or greater; preferably 10 to 270, and more preferably 40-270; and

q is an integer of 0-3.



These polymers are described in U.S. Pat. No. 5,468,477, which is hereby incorporated by reference. Most preferred is poly(dimethylsiloxane)-g-poly(isobutyl methacrylate), which is manufactured by 3-M Company under the tradename VS 70 IBM. This polymer may be purchased in the dry particulate form, or as a solution where the polymer is dissolved in one or more solvents such as isododecane. Preferred is where the polymer is in dry particulate form, and as such it can be dissolved in one or more of the liquids comprising the liquid carrier. This polymer has the CTFA name Polysilicone-6.

Another type of such a polymer comprises a vinyl, methacrylic, or acrylic backbone with pendant siloxane groups and pendant fluorochemical groups. Such polymers preferably comprise repeating A, C, D and optionally B monomers wherein:

A is at least one free radically polymerizable acrylic or methacrylic ester of a 1,1,-dihydroperfluoroalkanol or analog thereof, omega-hydrofluoroalkanois, fluoroalkylsulfonamido alcohols, cyclic fluoroalkyl alcohols, and fluoroether alcohols,

B is at least one reinforcing monomer copolymerizable with A,

C is a monomer having the general formula  $X(Y)_nSi(R)_{3-m}Z_m$  wherein

X is a vinyl group copolymerizable with the A and B monomers,

Y is a divalent linking group which is alkylene, arylene, alkarylene, and aralkylene of 1 to 30 carbon atoms which may incorporate ester, amide, urethane, or urea groups,

n is zero or 1;

m is an integer of from 1 to 3,

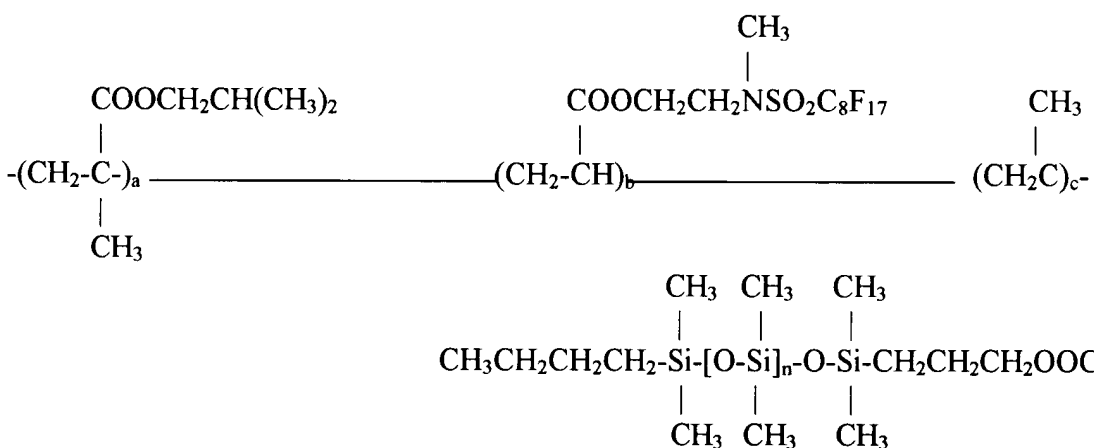
R is hydrogen,  $C_{1-4}$  alkyl, aryl, or alkoxy,

Z is a monovalent siloxane polymeric moiety; and

D is at least one free radically polymerizable acrylate or methacrylate copolymer.

Such polymers and their manufacture are disclosed in U.S. Pat. Nos. 5,209,924 and 4,972,037, which are hereby incorporated by reference. These polymers may be water soluble or oil soluble depending on the polymeric substituents. More specifically, the preferred polymer is a combination of A, C, and D monomers wherein A is a polymerizable acrylic or methacrylic ester of a fluoroalkylsulfonamido alcohol, and where D is a methacrylic acid ester of a C<sub>1-2</sub> straight or branched chain alcohol, and C is as defined above. Most preferred is a polymer having moieties of the general formula:

has the general formula:

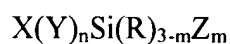


wherein each of a, b, and c has a value in the range of 1-100,000, and the terminal groups are selected from the group consisting of a C<sub>1-20</sub> straight or branched chain alkyl, aryl, and alkoxy and the like. These polymers may be purchased from Minnesota Mining and Manufacturing Company under the tradenames "Silicone Plus" polymers. Most preferred is poly(isobutyl methacrylate -co- methyl FOSEA) -g- poly(dimethylsiloxane) which is sold under the tradename SA 70-5 IBMMF.

Another suitable silicone acrylate copolymer is a polymer having a vinyl,

methacrylic, or acrylic polymeric backbone with pendant siloxane groups. Such polymers as disclosed in U.S. Pat. Nos. 4,693,935, 4,981,903, 4,981,902, and which are hereby incorporated by reference. Preferably, these polymers are comprised of A, C, and optionally B monomers wherein:

- 5        A is at least one free radically polymerizable vinyl, methacrylate, or acrylate monomer;  
         B, when present, is at least one reinforcing monomer copolymerizable with A,  
         C is a monomer having the general formula:



wherein:

- 10        X is a vinyl group copolymerizable with the A and B monomers;  
         Y is a divalent linking group;  
         n is zero or 1;  
         m is an integer of from 1 to 3;  
         R is hydrogen, C<sub>1-10</sub> alkyl, substituted or unsubstituted phenyl, C<sub>1-10</sub> alkoxy; and  
15        Z is a monovalent siloxane polymeric moiety.

Examples of A monomers are lower to intermediate methacrylic acid esters of C<sub>1-12</sub> straight or branched chain alcohols, styrene, vinyl esters, vinyl chloride, vinylidene chloride, acryloyl monomers, and so on.

- The B monomer, if present, is a polar acrylic or methacrylic monomer having at least  
20        one hydroxyl, amino, or ionic group (such as quaternary ammonium, carboxylate salt, sulfonic acid salt, and so on).

         The C monomer is as above defined. These types of silicone acrylate copolymers may also be water soluble or oil soluble depending on the substituent groups on the polymer.

Most preferred is where the film forming polymer comprises Polysilicone-6, which is a dry particulate material that may be used as is or solubilized in one or more ingredients that form the liquid carrier.

Examples of other suitable copolymers that may be used herein, and their method of manufacture, are described in detail in U.S. Pat. No. 4,693,935, Mazurek, U.S. Pat. No. 4,728,571, and Clemens et al., both of which are incorporated herein by reference. Additional grafted polymers are also disclosed in EPO Application 90307528.1, published as EPO Application 0 408 311, U.S. Pat. No. 5,061,481, Suzuki et al., U.S. Pat. No. 5,106,609, Bolich et al., U.S. Pat. No. 5,100,658, Bolich et al., U.S. Pat. No. 5,100,657, Ansher-Jackson, et al., U.S. Pat. No. 5,104,646, Bolich et al., U.S. Pat. No. 5,618,524, issued Apr. 8, 1997, all of which are incorporated by reference herein in their entirety.

## 2. Polymers from Ethylenically Unsaturated Monomers

Also suitable for use as film forming polymers are polymers made by polymerizing one or more ethylenically unsaturated monomers. The final polymer may be a homopolymer, copolymer, terpolymer, or graft or block copolymer, and may contain monomeric units such as acrylic acid, methacrylic acid or their simple esters, styrene, ethylenically unsaturated monomer units such as ethylene, propylene, butylene, etc., vinyl monomers such as vinyl chloride, styrene, and so on. Such polymers may be water soluble or dispersible, or oil soluble or dispersible in oil.

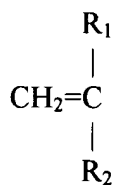
Preferred are polymers containing one or more monomers which are esters of acrylic acid or methacrylic acid, including aliphatic esters of methacrylic acid like those obtained with the esterification of methacrylic acid or acrylic acid with an aliphatic

alcohol of 1 to 30, preferably 2 to 20, more preferably 2 to 8 carbon atoms. If desired, the aliphatic alcohol may have one or more hydroxy groups. Also suitable are methacrylic acid or acrylic acid esters esterified with moieties containing alicyclic or bicyclic rings such as cyclohexyl or isobornyl, for example.

- 5           The ethylenically unsaturated monomer may be mono-, di-, tri-, or polyfunctional as regards the addition-polymerizable ethylenic bonds. A variety of ethylenically unsaturated monomers are suitable.

Examples of suitable monofunctional ethylenically unsaturated monomers include those of the formula:

10    I.



15

wherein  $R_1$  is H, a  $C_{1-30}$  straight or branched chain alkyl, aryl, aralkyl;  $R_2$  is a pyrrolidone, a  $C_{1-30}$  straight or branched chain alkyl, or a substituted or unsubstituted aromatic, alicyclic, or bicyclic ring where the substituents are  $C_{1-30}$  straight or branched chain alkyl, or COOM wherein M is H, a  $C_{1-30}$  straight or branched chain alkyl, pyrrolidone, or a substituted or unsubstituted aromatic, alicyclic, or bicyclic ring where the substituents are  $C_{1-30}$  straight or branched chain alkyl which may be substituted with one or more hydroxyl groups, or  $[(CH_2)_mO]_nH$  wherein m is 1-20, and n is 1-200.

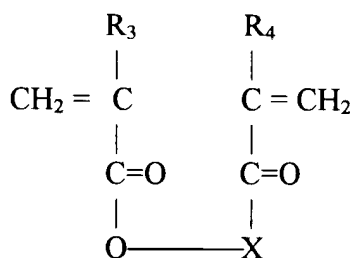
Preferably, the monofunctional ethylenically unsaturated monomer is of Formula

- 25    I, above, wherein  $R_1$  is H or a  $C_{1-30}$  alkyl, and  $R_2$  is COOM wherein M is a  $C_{1-30}$  straight or branched chain alkyl which may be substituted with one or more hydroxy groups.

More preferably, R<sub>1</sub> is H or CH<sub>3</sub>, and R<sub>2</sub> is COOM wherein M is a C<sub>1-10</sub> straight or branched chain alkyl which may be substituted with one or more hydroxy groups. In the preferred embodiment of the invention, the monofunctional ethylenically unsaturated monomer is a mixture of monomers of Formula I where in one monomer R<sub>1</sub> is H or CH<sub>3</sub> and R<sub>2</sub> is COOM where M is a C<sub>1-10</sub> alkyl, and where in the second monomer R<sub>1</sub> is H or CH<sub>3</sub>, and R<sub>2</sub> is COOM where M is a C<sub>1-10</sub> alkyl substituted with one or more hydroxy groups.

Di-, tri- and polyfunctional monomers, as well as oligomers, of the above monofunctional monomers may also be used in the composition. Suitable difunctional monomers include those having the general formula:

II.



wherein R<sub>3</sub> and R<sub>4</sub> are each independently H, a C<sub>1-30</sub> straight or branched chain alkyl, aryl, or aralkyl; and X is [(CH<sub>2</sub>)<sub>x</sub>O<sub>y</sub>]<sub>z</sub> wherein x is 1-20, and y is 1-20, and z is 1-100.

Particularly preferred are difunctional acrylates and methacrylates, such as the compound of formula II above wherein R<sub>3</sub> and R<sub>4</sub> are CH<sub>3</sub> and X is [(CH<sub>2</sub>)<sub>x</sub>O<sub>y</sub>]<sub>z</sub> wherein x is 1-4; and y is 1-6; and z is 1-10.

Particularly preferred are difunctional acrylates and methacrylates, such as the compound of formula II above wherein R<sub>3</sub> and R<sub>4</sub> are CH<sub>3</sub> and X is [(CH<sub>2</sub>)<sub>x</sub>O<sub>y</sub>]<sub>z</sub> wherein x is 2; and y is 1, and z is 4. The polymerizable compositions preferably contain 0.1-

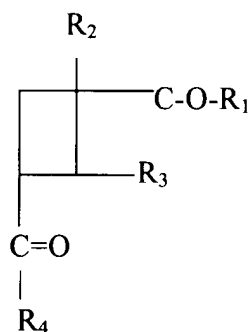
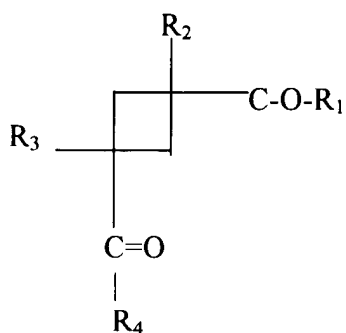
25%, preferably 0.5-20%, more preferably 1-15% by weight of a difunctional monomer.

Particularly preferred is where the difunctional monomer is an ethylene glycol dimethacrylate. Most preferred is where the difunctional monomer is tetraethylene glycol dimethacrylate.

- 5           Trifunctional and polyfunctional monomers are also suitable for use in the polymerizable monomer compositions of the invention. Examples of such monomers include acrylates and methacrylates such as trimethylolpropane trimethacrylate or trimethylolpropane triacrylate.

10           The polymers used in the compositions of the invention can be prepared by conventional free radical polymerization techniques in which the monomer, solvent, and polymerization initiator are charged over a 1-24 hour period of time, preferably 2-8 hours, into a conventional polymerization reactor in which the constituents are heated to about 60-175° C., preferably 80-100° C. The polymers may also be made by emulsion polymerization or suspension polymerization using conventional techniques. Also  
15           anionic polymerization or Group Transfer Polymerization (GTP) is another method by which the copolymers used in the invention may be made. GTP is well known in the art and disclosed in U.S. Patent Nos. 4,414,372; 4,417,034; 4,508,880; 4,524,196; 4,581,428; 4,588,795; 4,598,161; 4,605,716; 4,605,716; 4,622,372; 4,656,233; 4,711,942; 4,681,918; and 4,822,859; all of which are hereby incorporated by reference.

- 20           Particularly preferred are polymers of Formula I, above, which are cyclized, in particular, cycloalkylacrylate polymers or copolymers having the following general formulas:

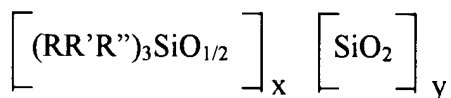


wherein  $R_1$ ,  $R_2$ ,  $R_3$ , and  $R_4$  are as defined above. Typically such polymers are referred to as cycloalkylacrylate polymers. Such polymers are sold by Phoenix Chemical, Inc. under the tradename Giovarez AC-5099M. Giovarez has the chemical name isododecane acrylates copolymer and the polymer is solubilized in isododecane.

### 3. Silicone Polymers

Also suitable are various types of water soluble or water insoluble (oil soluble) high molecular weight silicone polymers such as silicone gums, resins, and the like.

Suitable silicone resins include siloxy silicate polymers having the following general formula:





wherein R, R' and R'' are each independently a C<sub>1-10</sub> straight or branched chain alkyl or phenyl, and x and y are such that the ratio of (RR'R'')<sub>3</sub>SiO<sub>1/2</sub> units to SiO<sub>2</sub> units is 0.5 to 1 to 1.5 to 1.

5 Preferably R, R' and R'' are a C<sub>1-6</sub> alkyl, and more preferably are methyl and x and y are such that the ratio of (CH<sub>3</sub>)<sub>3</sub>SiO<sub>1/2</sub> units to SiO<sub>2</sub> units is 0.75 to 1. Most preferred is this trimethylsiloxo silicate containing 2.4 to 2.9 weight percent hydroxyl groups which is formed by the reaction of the sodium salt of silicic acid, chlorotrimethylsilane, and isopropyl alcohol. The manufacture of trimethylsiloxo silicate  
10 is set forth in U.S. patent nos. 2,676,182; 3,541,205; and 3,836,437, all of which are hereby incorporated by reference. Trimethylsiloxo silicate as described is available from Dow Corning Corporation under the tradename 2-0749 and 2-0747, which is a blend of about 40-60% volatile silicone and 40-60% trimethylsiloxo silicate. Dow Corning 2-0749 in particular, is a fluid containing about 50% trimethylsiloxo silicate and about 50%  
15 cyclomethicone. The fluid has a viscosity of 200-700 centipoise at 25° C., a specific gravity of 1.00 to 1.10 at 25° C., and a refractive index of 1.40-1.41. A similar siloxysilicate resin is available from GE Silicones under the tradename SR1000 and is a fine particulate solid material.

Another type of silicone resin suitable for use in the invention comprises the  
20 silicone esters set forth in U.S. Patent No. 5,725,845 which is hereby incorporated by reference in its entirety. Other polymers that can enhance adhesion to skin include silicone esters comprising units of the general formula  $R_aR_b^E\text{SiO}_{[4-(a+b)/2]}$  or  $R^{13}_xR^E_y\text{SiO}_{1/2}$  wherein R and R<sup>13</sup> are each independently an organic radical such as alkyl, cycloalkyl, or aryl, or, for example, methyl, ethyl, propyl, hexyl, octyl, decyl, aryl, cyclohexyl, and the

like, a is a number ranging from 0 to 3, b is a number ranging from 0 to 3, a+b is a number ranging from 1 to 3, x is a number from 0 to 3, y is a number from 0 to 3 and the sum of x+y is 3, and wherein R<sup>E</sup> is a carboxylic ester containing radical. Preferred R<sub>E</sub> radicals are those wherein the ester group is formed of one or more fatty acid moieties (e.g. of about 2, often about 3 to 10 carbon atoms) and one or more aliphatic alcohol moieties (e.g. of about 10 to 30 carbon atoms). Examples of such acid moieties include those derived from branched-chain fatty acids such as isostearic, or straight chain fatty acids such as behenic. Examples of suitable alcohol moieties include those derived from monohydric or polyhydric alcohols, e.g. normal alkanols such as n-propanol and branched-chain etheralkanols such as (3,3,3-trimethylolpropoxy)propane. Preferably the ester subgroup (i.e. the carbonyloxy radical) will be linked to the silicon atom by a divalent aliphatic chain that is at least 2 or 3 carbon atoms in length, e.g. an alkylene group or a divalent alkyl ether group. Most preferably that chain will be part of the alcohol moiety, not the acid moiety.

Preferably the silicone ester will have a melting point of no higher than about 90° C. It can be a liquid or solid at room temperature. Preferably it will have a waxy feel and a molecular weight of no more than about 100,000 daltons.

Silicone esters having the above formula are disclosed in U.S. patent no. 4,725,658 and U.S. patent no. 5,334,737, which are hereby incorporated by reference. Preferred silicone esters are the liquid siloxy silicates disclosed in U.S. patent no. 5,334,737, e.g. diisostearoyl trimethylolpropane siloxysilicate (prepared in Examples 9 and 14 of this patent), and dilauroyl trimethylolpropane siloxy silicate (prepared in

Example 5 of the patent), which are commercially available from General Electric under the tradenames SF 1318 and SF 1312, respectively.

Silicone gums or other types of silicone solids may be used provided they are soluble in the liquid vehicle. Examples of silicone gums include those set forth in U.S.

5 Patent No.6,139,823, which is hereby incorporated by reference. Preferred gums have a 600,000 to 1,000,000 centipoise at 25° C.

#### B. Natural Polymers

Also suitable for use are one or more naturally occurring water soluble or oil soluble polymeric materials such as resinous plant extracts including such as rosin,  
10 shellac, and the like.

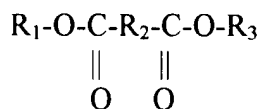
#### IV. Other Ingredients

##### A. Plasticizers

It is desirable to incorporate one more plasticizers into the composition. Since the preferred compositions tend to have a lower viscosity when compared to standard  
15 products of this nature, the plasticizer will improve the spreadability and application of the composition to the surface to which it is applied. The preferred compositions contain one or more plasticizers in an amount sufficient to improve spreadability and application of the composition when compared to the same composition without the plasticizer.

Preferably the plasticizer is found in the oil phase of the emulsion. Suggested ranges of  
20 plasticizers range from about 0.01-20%, preferably about 0.05-15%, more preferably about 0.1-10% by weight of the total composition. A variety of plasticizers are suitable including Suitable plasticizers include glyceryl, glycol, and citrate esters as disclosed in U.S. Patent No. 5,066,484, which is hereby incorporated by reference. Examples of such

esters include glyceryl tribenzoate, glyceryl triacetate, acetyl tributyl citrate, dipropylene glycol dibenzoate, and the like. Also suitable, are plasticizers of the following general formula:



10 wherein  $R_1$ ,  $R_2$ , and  $R_3$  are each independently a  $C_{1-20}$  straight or branched chain alkyl or alkylene which may be substituted with one or more hydroxyl groups. Preferably,  $R_1$  is a  $C_{3-10}$  straight or branched chain alkyl;  $R_2$  is a  $C_{2-8}$  alkyl which may be substituted with one or more hydroxyl groups; and  $R_3$  is a  $C_{3-10}$  straight or branched chain alkyl.

Examples of such compounds include dioctyl malate, diisopropyl adipate, dibutyl  
15 adipate, dibutyl sebacate, dioctyl azelate, dioctyl succinate, dioctyl fumarate, and the like. Preferred is where  $R_1$  and  $R_3$  are a branched  $C_8$  alkyl,  $R_2$  is a  $C_2$  alkyl substituted with one hydroxy group, which is dioctyl malate.

Preferred plasticizers are the glycerol, glycol and citrate esters, in particular acetyl tributyl citrate. Generally such plasticizers are oil soluble and become part of the oil  
20 phase of the composition.

#### B. Viscosity Modifiers

It may also be desirable to include one or more viscosity modifiers in the composition. As previously noted the viscosity modifiers are not organic, solid, non-polymeric fatty phase gelling agents as mentioned above. In particular, since the  
25 preferred compositions exhibit a viscosity that is slightly reduced, inclusion of the viscosity modifiers, which will, specifically increase viscosity, cause the composition to



have more body and less tendency to run or drip when applied to the desired surface.

Suggested ranges of such viscosity modifiers are about 0.01-60%, preferably about 0.05-50%, more preferably about 0.1-45% by weight of the total composition. Preferred are where the viscosity modifiers are not waxes or wax like materials. The term "wax"

5 means waxy materials such as natural or synthetic waxes such as synthetic wax, polyethylene, rice wax, ceresin, carnauba, and the like. More preferred is where such viscosity modifiers form part of the oil phase of the emulsion. Suitable viscosity modifiers include natural or synthetic montmorillonite minerals such as hectorite, bentonite, and quaternized derivatives thereof which are obtained by reacting the  
10 minerals with a quaternary ammonium compound, such as stearylquaternium bentonite, hectorites, quaternized hectorites such as Quaternium-18 hectorite, attapulgite, carbonates such as propylene carbonate, bentonites, and the like. Particularly preferred is Quaternium-18 hectorite.

Also suitable as the viscosity modifier are various polymeric compounds known  
15 in the art as associative thickeners. Suitable associative thickeners generally contain a hydrophilic backbone and hydrophobic side groups. Examples of such thickeners include polyacrylates with hydrophobic side groups, cellulose ethers with hydrophobic side groups, polyurethane thickeners. Examples of hydrophobic side groups are long chain alkyl groups such as dodecyl, hexadecyl, or octadecyl; alkylaryl groups such as  
20 octylphenyl or nonylphenyl

Another type of viscosity modifier that may be used in the compositions are silicas, silicates, silica silylate, and derivatives thereof. These silicas and silicates are generally found in the particulate form. Particularly preferred is silica.

The viscosity modifiers may also be water soluble or water insoluble (e.g. oil soluble) and form part of the oil phase or the water phase.

In the most preferred embodiment of the invention, the compositions are free of wax viscosity modifiers, meaning waxes such as synthetic wax, castor wax, ceresin, rice wax, and the like.

The invention will be further described in connection with the following examples which are set forth for the purposes of illustration only.

#### EXAMPLE 1

An emulsion composition for making up the eyelashes was prepared as follows:

		w/w%
	Dimethicone 1.0cs	20.57
	Isododecane	23.85
15	3M VS-70 vinyl silicone (Polysilicone-6)	20.35
	Dibutyl Adipate	2.40
	Silica	6.00
	Quaternium-18 Hectorite 10%, Isododecane 89%	18.00
	Propylene Carbonate	1.00
20	Cetyl dimethicone copolyol	0.3
	Water	5.00
	FD&C Blue #1	1.44
	FD&C Yellow #5	0.60
	D&C Green #5	0.05
25	FD&C Red #40	1.44

The composition was prepared by combining the water soluble pigments and water phase and mixing well. The remaining oil phase ingredients were separately mixed. Both phases were combined and emulsified to form the final composition, which was a eyelash color in a rich black shade.

While the invention has been described in connection with the preferred embodiment, it is not intended to limit the scope of the invention to the particular form

set forth but, on the contrary, it is intended to cover such alternatives, modifications, and equivalents as may be included within the spirit and scope of the invention as defined by the appended claims.

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